HYDROGEN GASIFICATION OF OXIDIZED CARBONS

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INTRODUCTION

Hydrogen gasification of carbon has been studied less intensively than steam and carbon dioxide gasification over the past twenty years, although the carbon-hydrogen reaction is important in producing synthetic fuels from coal. In addition to being a direct, selective route to methane, the carbon-hydrogen reaction reduces the endothermicity of steam gasification. More importantly, hydrogen gasification can be studied as a model system to better understand fundamental aspects of steam gasification such as catalyst behavior and hydrogen inhibition. Also, gasification in pure hydrogen provides a unique environment for the accounting of oxygen present in the catalyst and carbon during gasification.

Alkali carbonates are effective catalysts for hydrogen gasification of coal chars and carbon black [1-3] but not of graphite [4]. The presence of oxygen during hydrogen gasification is also reported to accelerate methane formation. For uncatalyzed gasification of wood char, Blackwood [5] reported that rate is linearly related to oxygen content of the char. For carbon films, Cao and Back [6] reported that the addition of 0.1% oxygen to the hydrogen stream accelerated methane formation considerably.

The nature of oxygen-containing groups on carbon surfaces has been studied for many years; such surface groups can generally be categorized as acidic, neutral, basic, or inert [7]. Carboxyl, phenol, and lactone groups have been proposed [8] as acidic complexes; they are formed by oxidation at temperatures around 400°C and decompose to give CO_2 above 500°C. Carbonyl and quinone groups are neutral or weakly acidic and decompose to CO around 750°C [9]. Basic surface groups include chromene or pyrone complexes and can persist on the surface at temperatures above 1000°C [10]. Aromatic ethers are generally inert and make up the majority of surface oxygen [11].

Over the past several years we have conducted experimental studies to better understand alkali carbonate catalyst behavior in hydrogen gasification and to determine the effect of oxygen on gasification rate. We observe [12,13] that catalyst behavior in hydrogen gasification is similar to that in steam gasification, leading us to believe that catalyst-carbon interactions are of primary importance in gasification and that catalyst behavior is relatively unaffected by reactant gas. Thus hydrogen is a suitable model environment for studying catalyst behavior. One exception, however, is that higher rates of catalyst loss are observed in hydrogen [12] than in steam [14].

For uncatalyzed gasification, we have shown [15] that partial combustion of carbon black prior to exposure to hydrogen enhances methane formation rate, while high temperature pretreatment (degassing) drastically reduces reaction rate. These results, shown in Figure 1, arise from the addition or removal of active surface oxygen groups and from thermal annealing of the carbon active sites. Via pH measurements [15], we have found that partial combustion at

400°C fixes acidic groups on the carbon surface. Gasified and degassed carbons contain a predominance of basic groups.

The paper presents further studies of the role of surface oxygen and thermal treatments in both catalyzed and uncatalyzed hydrogen gasification. In this work, a second carbon substrate and oxidation by HNO_3 are investigated. Nitric acid produces a variety of groups on carbon, but does not alter the carbon structure. Comparison of results for the different carbons and two methods of oxidation provides clarification of the role of oxygen. X-ray photoelectron spectroscopy (XPS) provides further information.

EXPERIMENTS

Apparatus- Gasification experiments, including high temperature pretreatment and partial combustion, were carried out in a high-pressure fixed bed differential reactor described in detail elsewhere [12]. Reaction rates were measured by timed collection of product gas, which typically consisted only of methane in hydrogen. All gasification experiments, unless otherwise indicated, were carried out in pure hydrogen (Airco, 99.999%) at 500 psig and a flow rate of 310 ml (STP) per minute. Gasification temperatures ranged from 775°C to 865°C and typical carbon sample sizes ranged from 40-110 mg. The reactor was evacuated to 0.01 torr during initial heatup; hydrogen flow was started when sample temperature reached 500°C. For the gasification rates measured, transport resistances are negligible [16].

Surface analyses of solid reactants were carried out on a Perkin-Elmer PHI 5400 X-ray Photoelectron Spectrometer located in the Composite Materials and Structures Center at Michigan State University. To pretreat, oxidize, and gasify carbons for XPS analyses, a separate high-vacuum chamber has been constructed. The chamber is capable of attaining vacuum to 10^{-8} torr and pressure to 30 psig at room temperature, and vacuum to 10^{-8} torr at 1000°C. The chamber is equipped with a sample introduction attachment which allows samples to be transferred to the XPS without exposure to atmosphere.

Solid Reactants- The carbon black was Raven 16 furnace black (Cities Service, Co., Columbian Chemicals) produced by oxygen-deficient combustion of heavy oil. It is a graphitic carbon black with a particle size of about 60 nm. X-ray diffraction shows crystallite dimensions of L_a=3.7 nm and L_c=3.0 nm. The initial N_2-BET surface area is about 15 m^2/g; BET surface area increases almost linearly with conversion during gasification to a value of 400 m^2/g at 60% conversion. Ultimate analysis of the carbon black is given in Table 1.

The second carbon was a 50-200 mesh coconut charcoal (Fisher Sci.) which was washed in concentrated HCl at room temperature to reduce its ash content prior to gasification. The char is noncrystalline and has a N_2-BET surface area of 750 m^2/g which remains essentially constant during reaction. Ultimate analysis of the char is given in Table 1. Most noteworthy is the higher oxygen content of the char as compared to carbon black.

In all experiments, the order of treatment was degassing, oxidation, and impregnation. Degassing consisted of heating at 1273 K for 15 hours at 0.01 torr. Nitric acid oxidation was accomplished by placing the sample in 70% HNO_3 at room temperature for 24 hours, washing thoroughly with doublydistilled deionized water, and oven drying at 120°C. Potassium carbonate was deposited on the carbons by wet impregnation. A K/C ratio of 0.02, corresponding to about 10 wt% K_2CO_3, was used in all catalyzed experiments.

RESULTS

Gasification results are reported as reaction rate per unit total surface area (TSA) versus carbon conversion. While rates are best represented per unit active surface area, no measurement of active surface area was made in this study. Because the TSA for both carbon black and char are well characterized and depend only on conversion, this basis is equivalent, for comparative purposes, to a weight basis. Total surface area is used instead of weight to eliminate consideration of effects of TSA on gasification rate.

Carbon Black - The effect of degassing at 1273 K on carbon surface composition was determined via XPS and is shown in Figure 2. Degassing lowers oxygen surface content from over 5% to 0.26%; the residual concentration is close to that of oxygen in the bulk solid.

The effects of pretreatment and HNO_3 oxidation on uncatalyzed hydrogen gasification rate are shown in Figure 3. Oxidation of as-received (fresh) carbon black results in approximately a 30% increase in methane formation rate. Degassing reduces the rate approximately six-fold; subsequent exposure to nitric acid results in only a slight rate enhancement (5-10%) which cannot be discerned in the Figure.

These results are compared to earlier gasification rate measurements following oxidation via partial combustion in oxygen at 400°C (Figure 1). Partial combustion prior to hydrogen exposure results in approximately a two-fold increase in methane formation rate for both fresh and degassed carbon black.

Results of pretreatment and HNO_3 oxidation on catalyzed gasification rate are shown in Figure 4. K_2CO_3 strongly catalyzes hydrogen gasification of all samples; HNO_3 oxidation enhances catalyzed methane formation from fresh and degassed samples more significantly than uncatalyzed methane formation.

Coconut Char - XPS analysis of the char indicates that initial surface oxygen content is 4.1%, close to the value for bulk char of 3.4%. Uncatalyzed gasification rates for coconut char exposed to degassing and HNO_3 oxidation are shown in Figure 5. In contrast to carbon black, degassing only reduces reaction rate by a factor of two. Nitric acid oxidation significantly increases rate for both fresh and degassed samples; for the degassed sample oxidation increases rate almost to the value of that for fresh char. At high conversion the rates of all samples converge; the effects of surface treatments apparently decay as carbon is consumed.

Catalyzed gasification rates for coconut char exposed to the same degassing and oxidation are shown in Figure 6. Degassing has essentially no effect on the catalyzed hydrogen gasification rate, and HNO_3 oxidation enhances rate about two-fold for both fresh and degassed chars.

DISCUSSION

Uncatalyzed gasification - In an earlier paper [15], we postulated that acidic groups on the carbon black surface decompose to form "nascent" or active sites at which hydrogen gasification most readily occurs. These nascent sites are consumed as carbon black reacts, resulting in the observed decrease in gasification rate. Thermal degradation of nascent sites does not occur at gasification temperatures, as evidenced by an experiment in which carbon black was heated to 865°C for four hours in helium. Upon exposure to hydrogen, the reaction rate observed was the same as that of a sample directly heated to 865°C.

High temperature (1270 K) degassing desorbs CO_2 and CO from acidic groups and then thermally "anneals" the nascent sites formed, thus resulting in a much lower gasification rate. The XPS results indicate that all excess surface oxygen is removed. Gasification activity following degassing, which remains constant with carbon conversion, is attributed to basic oxygen groups in bulk carbon which are exposed as carbon is gasified. These groups must also facilitate carbon gasification although at a much slower rate. Finally, X-ray diffraction patterns are identical for fresh and degassed carbons, indicating that "annealing" is a surface process only.

Partial oxidation in oxygen at 400°C produces significant new surface area in carbon black, as about 10% of the solid is gasified by oxygen. In addition, acidic oxygen groups are fixed on the surface. Upon heating to hydrogen gasification temperatures (830-865°C), these acidic sites decompose to give nascent sites at which hydrogen gasification takes place. Thus partial combustion enhances methane formation for both fresh and degassed carbon black via the creation of active sites from acidic surface groups on newly exposed surface area.

Nitric acid oxidation produces both acidic and basic oxygen groups and gives different results than partial combustion. Oxidation of fresh carbon black somewhat enhances methane formation rate; acidic groups formed in oxidation again form nascent sites upon heating in hydrogen. Upon degassing, however, the carbon surface is no longer susceptible to nitric acid oxidation, and only slight methane rate enhancement is observed following oxidation of the degassed carbon. Little evolution of NO_2 occurred during oxidation; the degassed carbon black surface is apparently not susceptible to oxidation.

The coconut char studied has significantly different structure and oxygen content and exhibits much different gasification behavior than carbon black. The nearly constant gasification rate of the char over the conversion range studied suggests that the high bulk oxygen content and amorphous structure of the char provide new active sites for gasification as carbon is consumed.

The effect of degassing on gasification rate is much less for the char than for carbon black. We propose that this also results from the amorphous nature and high bulk oxygen content of the char. Degassing removes only surface-adsorbed groups and does not affect bulk oxygen, which is present in much higher levels than in carbon black (Table 1). Also, because the char is amorphous and thus so many carbon atoms are potential reactive sites, thermal annealing does not destroy as large a fraction of active sites in the char as in carbon black. Thus, while acidic surface groups are desorbed during degassing and the nascent sites associated with them likely annealed, there are enough reactive sites and bulk oxygen remaining that char reactivity is only moderately reduced.

Both fresh and degassed char show significant gasification rate enhancement upon oxidation in HNO_3. The large quantity of NO_2 evolved during oxidation indicates extensive oxidation of the surface, which is directly attributable to the noncrystalline nature of the char. The increase in acidic group concentration from oxidation results in accelerated methane formation following oxidation.

Catalyzed Gasification - The results in Figures 4 and 6 for carbon black and coconut char, respectively, suggest that the neutral and basic groups (carbonyl and pyrone/chromene) interact with K_2CO_3 and result in catalytic enhancement of reaction rate. Hydrogen gasification of degassed carbon black, which contains only stable basic groups arising from bulk oxygen, is strongly catalyzed by K_2CO_3; oxidation by HNO_3 further enhances the catalyst activity. Partial combustion at 400°C does not enhance the K_2CO_3-catalyzed gasification rate of degassed carbon black [15], indicating that nascent sites formed by desorption of acidic groups do not interact with the catalyst.

For coconut char, there is essentially no difference in catalyzed gasification rate of fresh and degassed samples. This indicates that surface groups desorbed during degassing are not important for the catalytic reaction; instead it appears that basic groups arising from bulk oxygen, which are not affected by degassing, interact with the catalyst. Nitric acid oxidation, which results in a significant increase in all types of oxygen groups, also results in a significant enhancement in catalyzed rate.

The nature of interaction between surface carbonyl and basic groups and K_2CO_3 is not yet understood. It is possible that surface oxidation simply allows catalyst to better wet and disperse on the carbon during hydrogen gasification. It has been observed that surface oxygen stabilizes catalyst on the surface during gasification; catalyst loss experiments indicate that catalyst loss is more rapid for degassed samples than fresh carbon and slower for oxidized samples than for fresh. Stabilizing of catalyst, however, may not enhance gasification rate. Finally, it is possible that surface oxygen may participate in one of the M-O- surface oxides currently under investigation as possible active catalyst forms [17].

In summary, it is apparent that hydrogen gasification rate is influenced by the treatments implemented. This is not to imply, however, that other factors are not important: for instance, the observations of Yang and Duan [18], who analyzed etch pits formed in hydrogen and oxygen and found that hydrogen produces hexagonal basal plane edges while oxygen produces arm-chair edges, could explain at least some gasification behavior. Further work, including extensive XPS studies, will provide more insight into the importance of oxygen in the reaction.

CONCLUSIONS

High temperature degassing and nitric acid oxidation have significant effects on the hydrogen gasification rate. For graphitic carbon black, surface annealing of nascent sites during degassing most strongly affects gasification activity, with oxidation having a lesser effect. This results from the fact that most oxygen and thus most active sites are initially on the carbon surface; once these sites are eliminated gasification is slowed. For uncatalyzed coconut char, degassing and nitric acid oxidation have opposite effects of about the same magnitude. The high bulk oxygen content makes initial removal of surface oxygen during degassing relatively unimportant; the amorphous char structure results in extensive oxidation which facilitates an increase in gasification rate.

Uncatalyzed hydrogen gasification is proposed to occur at nascent sites created by desorption of CO_2 from acidic surface groups, and to a much lesser extent at the basic groups formed from bulk carbon. Catalyzed gasification is proposed to occur via interaction of catalyst with basic surface groups.

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TABLE 1
ULTIMATE ANALYSIS OF REACTANTS

	Carbon Black	Coconut Char
Moisture, %	0.46	1.02
Carbon, %	96.92	91.82
Hydrogen, %	0.27	0.43
Nitrogen, %	0.29	1.81
Sulfur, %	1.54	0.06
Ash, %	0.31	1.48
Oxygen (diff), %	0.21	3.38

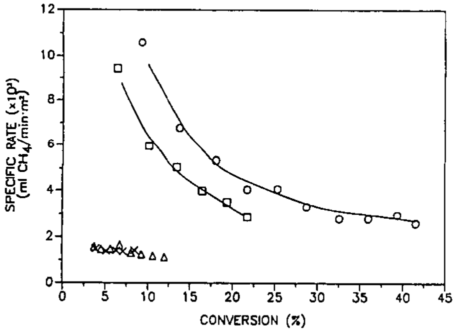

Figure 3. Uncatalyzed Carbon Black, 865°C, 500 psi H_2. (□)–Fresh; (○) HNO_3 oxidized, (Δ)–Degassed; (×)–Degassed, HNO_3 oxidized.

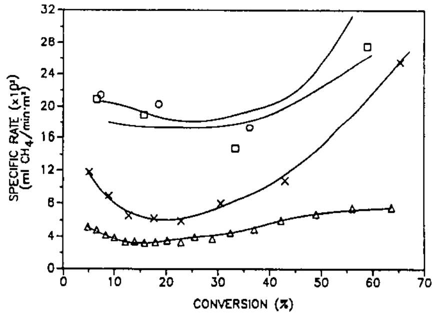

Figure 4. K_2CO_3–Catalyzed Carbon Black, 865°C, 500 psi H_2, K/C=0.02. (□)–Fresh; (○)–Oxidized, impreg.; (Δ)–Degassed, impreg. (×)–Degassed, oxidized, impregnated.

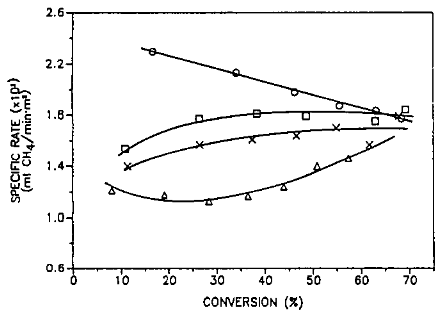

Figure 5. Uncatalyzed Coconut Charcoal, 865°C 500 psi H_2. (□)–Fresh; (○)–HNO_3 oxidized, (Δ)–Degassed; (×)–Degassed, HNO_3 oxidized.

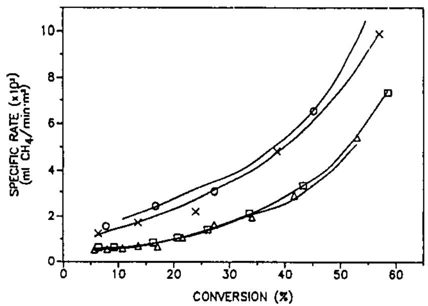

Figure 6. K_2CO_3–Catalyzed Coconut Charcoal, 775°C, 500 psi H_2, K/C=0.02. (□)–Fresh; (○)–Oxidized, impreg.; (Δ)–Degassed, impreg., (×)–Degassed, oxidized, impregnated.

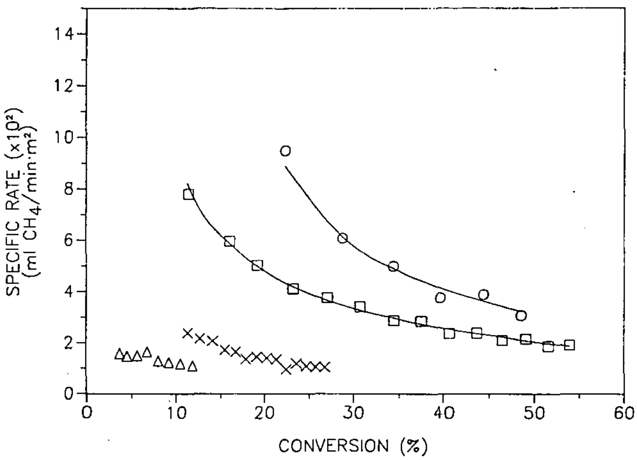

Figure 1. Uncatalyzed Carbon Black, 865°C, 500 psi H_2. (□)–Fresh; (o)–O_2 400°C; (△)–Degassed; (×)–Degassed, O_2 400°C.

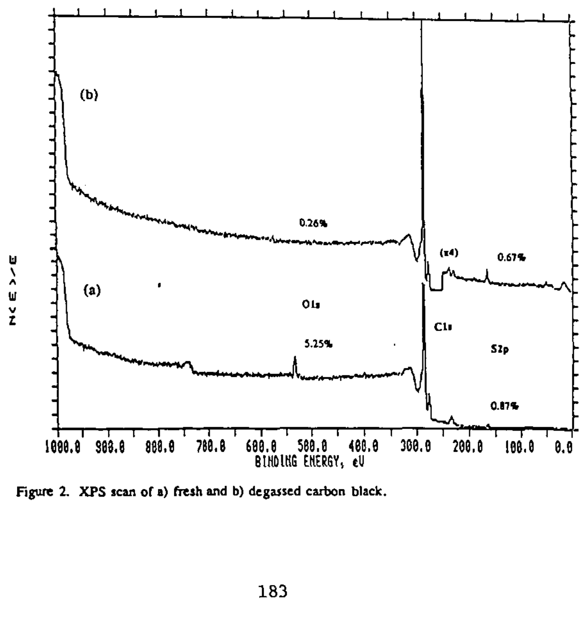

Figure 2. XPS scan of a) fresh and b) degassed carbon black.